



Dependency of simultaneous Cr(VI), Cu(II) and Cd(II) reduction on the cathodes of microbial electrolysis cells self-driven by microbial fuel cells

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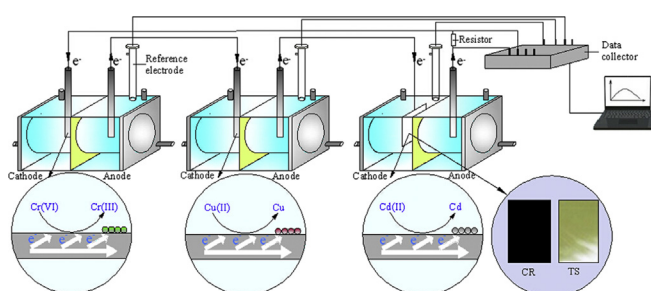
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HIGHLIGHTS

- Two stack MFCs with each reducing Cr(VI)/Cu(II) can self-drive MECs reducing Cd(II).
- Two MFCs in serial was superior to the parallel configuration for metal reduction.
- Titanium sheet instead carbon rod as cathodes of MECs proceeded Cd(II) reduction.
- A decrease in cathode volume in two MFCs benefited to system performance.

GRAPHICAL ABSTRACT



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ABSTRACT

Microbial fuel cells (MFCs) using either Cr(VI) (MFCs_{Cr}) or Cu(II) (MFCs_{Cu}) as a final electron acceptor, are stacked to self-drive microbial electrolysis cells (MECs) using Cd(II) (MECs_{Cd}) as an electron acceptor for simultaneous reduction of Cr(VI) in MFCs_{Cr}, Cu(II) in MFCs_{Cu} and Cd(II) in MECs_{Cd} with no external energy consumption. Titanium sheet (TS) and carbon rod (CR) as the cathodes of MECs_{Cd} are assessed for efficient system performance. MFCs_{Cr} and MFCs_{Cu} in series is superior to the parallel configuration, and higher Cd(II) reduction along with simultaneous Cr(VI) and Cu(II) reduction supports TS function as a good cathode material. Conversely, CR can not entirely proceed Cd(II) reduction in MECs_{Cd} despite of more Cr(VI) and Cu(II) reduction in the same serial configuration than either system alone. While a decrease in cathode volume in both MFCs_{Cr} and MFCs_{Cu} with serial connection benefits to reduction of Cr(VI) in MFCs_{Cr} and Cu(II) in MFCs_{Cu}, Cd(II) reduction in MECs_{Cd} is substantially enhanced under a decrease in cathode volume in individual MFCs_{Cr} and serially connected with volume-unchanged MFCs_{Cu}. This study demonstrates simultaneous Cr(VI), Cu(II) and Cd(II) recovery from MFCs_{Cr}-MFCs_{Cu}-MECs_{Cd} self-driven system is feasible, and TS as the cathodes of MECs_{Cd} is critical for efficient system performance.

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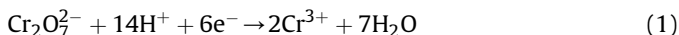
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1. Introduction

Heavy metals of Cr(VI), Cu(II) and Cd(II) have been extensively found in electroplating wastewaters which severely contaminate surfacewater and groundwater as well as soils if not properly treated [1,2]. Conventional techniques involving physical, chemical/electrochemical and biological technologies can recover the metals inside [1–4]. The high cost and serious second pollution, as well as great energy consumption urge a turn to environmental friendly and cost-effective strategies. Microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) are regarded as promising technologies to achieve sustainable wastewater treatment with simultaneous value-added products and clear energy generation [5–8]. MFCs have been used for recovery of various metals including Cr(VI) [9–12], Cu(II) [13–17], Fe(III) [18,19], V(V) [20], Se(IV) [21] and Cd(II) [22]. Applying voltages in MECs can recover Cu, Pb, Cd, Co and Zn [23,24]. Both of them broaden the scope of bioelectrochemical technologies for metal recovery from wastes and wastewaters. The main challenges include only recovering single metals using MFCs/MECs, and/or requiring energy consumption in MECs. While low power density of MFCs and difficulty for reactor scaling-up have been and will continue to be primary barriers for practical implementation of MFCs, in situ utilization of electricity generated from MFCs might bring in new opportunities because of its many unique features [8,25]. Together with considering the recovery of single Cr(VI), Cu(II) or Cd(II) using individual MFCs or MECs [9–17,22,23], there are still remaining challenges for using these approaches, such as recovering multiple metals, in situ utilization of power from MFCs, and minimizing or requiring no external power supply for MECs processes.

Aqueous Cr(VI) and Cu(II) can be theoretically reduced to Cr(III) and pure Cu at potentials of 1.33 V and 0.34 V (vs. standard hydrogen electrode, SHE), respectively whereas Cd(II) is reduced to Cd at a negative potential of -0.52 V (vs. SHE) under standard conditions by the following reactions of (1)–(3):



Considering the potential of $\sim(-0.30$ V) (vs. SHE) using acetate as a fuel at the anodes of bioelectrochemical systems [5], either Cr(VI) or Cu(II) reduction at the cathodes can occur spontaneously with acetate oxidation at the anodes in comparison with the requirement of external energy input for proceeding with a sufficient rate for Cd(II) reduction at the cathodes. The MFCs with Cr(VI) (MFCs_{Cr}) and Cu(II) (MFCs_{Cu}) reduction might thus power the MECs for Cd(II) reduction (MECs_{Cd}), in which not only Cr(VI), Cu(II) and Cd(II) are simultaneously recovered, but also power from MFCs is in-situ utilized for MECs and thus avoids the need for external energy input. Despite of the extensive exploration of MFCs integrated with either conventional processes or newly developed MECs for wastewater treatment with simultaneous hydrogen evolution, alkali production, cobalt and zinc recovery, or CO₂ reduction [8,26–35], to date, no essential attention has been paid to the MFCs_{Cr}–MFCs_{Cu}–MECs_{Cd} self-driven system as a promising technology for simultaneous Cr(VI), Cu(II) and Cd(II) reduction.

Electrode potential is one of the most important parts of MECs where different chemical products generation and hydrogen evolution may simultaneously occur [29,36–38]. For soluble metals reduction on the cathodes, a certain concentration of high soluble metals such as Cu(II) > 200 mg L⁻¹ at acidic conditions can preserve

fast mass transfer. The overpotential for this metal reduction is thus low [13–15]. However, reduction of metal ions at low concentrations in MECs can compete with hydrogen evolution or oxygen reduction, either of which heavily depends on electrode materials [13,24,37,38]. As a consequence, the reduction of metals at low concentrations is indirectly related with electrode material via hydrogen evolution or oxygen reduction. In addition, reduction of metal ions such as Cr(VI) under the mediation of dissolved oxygen is reasonably related with cathode materials [12]. In linkage with the more negative potential of -0.52 V for Cd(II) reduction than that for hydrogen evolution under standard conditions, reduction of Cd(II) at comparatively low concentrations may unavoidably compete with hydrogen evolution on the cathodes of MECs. Various material cathodes of MECs_{Cd} will thus to some extent affect the performance of itself as well as the connected MFCs_{Cr} and MFCs_{Cu}. In view of reaction dynamics in cells, high anode potentials can enhance the kinetics of substrate oxidation by providing a high driving force for microbe-to-electrode extracellular electron transfer. Similar considerations in principle hold for the cathodic reactions where low potentials are expected to yield better performances. The larger the difference between anode and cathode potentials, the higher the external energy input to the MECs. Various material cathodes of MECs_{Cd} may exhibit different overpotentials and thus diverse performances of this self-driven MFCs_{Cr}–MFCs_{Cu}–MECs_{Cd} system. In addition, electrons supplied on the cathodes of MECs_{Cd} are reasonably affected by current generation from both MFCs_{Cr} and MFCs_{Cu}, and a higher circuit current or a flow of more electrons will benefit to Cr(VI), Cu(II) and Cd(II) reduction in this system [7].

Carbon rod (CR) and titanium sheet (TS) have been used as the cathodes/anodes of either MECs or MFCs individually [36,39,40]. However, it is still not clear whether these materials can be necessarily used as the cathodes of MECs_{Cd} for sufficiently removing multiple metals of Cd(II) in MECs_{Cd}, Cr(VI) in MFCs_{Cr} and Cu(II) in MFCs_{Cu}, respectively. Exploring more efficient cathodes of MECs_{Cd} can reveal the complex mutual interactions between MECs_{Cd} and the adjacent MFCs_{Cr} and MFCs_{Cu}, and is thus essential for bilateral performances for efficient reduction of Cd(II) in MECs_{Cd}, Cr(VI) in MFCs_{Cr} and Cu(II) in MFCs_{Cu}.

Stack MFCs in series can increase voltage output whereas parallel stack MFCs increase circuit current [41–43], either of which may benefit to the adjacent MECs performance [29,30]. In terms of MECs_{Cd} self-driven by MFCs_{Cr} and MFCs_{Cu}, stack MFCs_{Cr} and MFCs_{Cu} in series or parallel connection can reasonably output different voltages and currents, and thus lead to different reduction of Cr(VI) in MFCs_{Cr}, Cu(II) in MFCs_{Cu} and Cd(II) in MECs_{Cd}. A better understanding of stack MFCs_{Cr} and MFCs_{Cu} will enable better design of MFCs_{Cr} and MFCs_{Cu} to power MECs_{Cd} and allow more efficient reduction of Cr(VI), Cu(II) and Cd(II) in this self-driven system.

Performance of MFCs is volume-dependent since a change in working volume in MFCs can change the distance between the electrodes and thus alter their internal resistance [44–47]. In the case of stack MFCs_{Cr} and MFCs_{Cu} as well as the connected MECs_{Cd}, a change in the working volume of either MFCs_{Cr} or MFCs_{Cu} as well as both can reasonably affect the performance of all MFCs_{Cr}, MFCs_{Cu} and MECs_{Cd}. Considering the benefit of appropriately close electrode spacing for less internal resistance and thereby improvement of MFC performance [44–46], a decrease in the working volume of either MFCs_{Cr} or MFCs_{Cu} as well as both is expected to enhance simultaneous reduction of Cr(VI) in MFCs_{Cr}, Cu(II) in MFCs_{Cu}, and Cd(II) in MECs_{Cd}.

In this study a truly integrated MFCs_{Cr}–MFCs_{Cu}–MECs_{Cd} self-driven system was successfully designed, which not only recovered energy from wastewaters through the anodes of both MFCs_{Cr}

and MFCs_{Cu}, and in-situ utilized this energy to drive MECs_{Cd}, and thus avoided the need for external energy input in MECs_{Cd}, but also achieved simultaneous recovery of multiple metals including Cr(VI), Cu(II) and Cd(II). CR and TS as the cathodes of MECs_{Cd} were assessed for efficient system performance. Effect of cathode working volume in MFCs_{Cr} and MFCs_{Cu} in series or parallel connection was investigated. System performance was evaluated with respect to multiple parameters including Cr(VI), Cu(II) and Cd(II) reduction, yields of Cr (Y_{Cr}), Cu (Y_{Cu}) and Cd (Y_{Cd}), hydrogen production, anodic coulombic efficiencies (CE) in terms of Cr (CE_{Cr}), Cu (CE_{Cu}) and Cd (CE_{Cd}), cathodic coulombic efficiencies (η) in terms of Cr (η_{Cr}), Cu (η_{Cu}) and Cd (η_{Cd}), as well as system efficiency (η_{sys}). The results obtained were used to outline, for the first time, a conceptual model that describes the importance of cathode material of MECs_{Cd} on efficient performance of self-driven MFCs_{Cr}–MFCs_{Cu}–MECs_{Cd} system, which needs to be considered for applicable recovery of multiple metals from electroplating wastewaters as subsequently discussed.

2. Materials and methods

2.1. Reactor setup

Two-chamber MFCs and MECs (duplicates) were used in all experiments, with the chambers separated by a cation exchange membrane (CEM) (CMI-7000 Membranes International, Glen Rock, NJ). Graphite felt (Sanye Co., Beijing, China) was used as the anodes of all MFCs_{Cr}, MFCs_{Cu} and MECs_{Cd}. Carbon rod (CR, Chijiu Duratight Carbon Co., Qingdao, China) with a projected surface area of 12 cm² was used as the cathodes of MFCs_{Cr} and MFCs_{Cu}. Either CR or TA1 titanium sheet (TS, 99.9%, Qingyuan Co., China) was served as the cathodes of MECs_{Cd} with a same projected surface area of 12 cm² and evaluated for their suitability as the cathodes. These materials were cleaned before tests using 0.5 M H₂SO₄.

2.2. Inoculation and operation

The anode was inoculated from the primary clarifier of Lingshui Wastewater Treatment Plant in Dalian, China, as previously reported [10]. For the initial acclimation, the anolyte was composed of wastewater equivalently mixed with a nutrient solution containing (g L⁻¹) sodium acetate, 1.0; KH₂PO₄, 4.4; K₂HPO₄, 3.4; NH₄Cl, 1.3; KCl, 0.78; MgCl₂, 0.2; CaCl₂, 0.0146; NaCl, 0.5; trace vitamins and minerals [24]. After 4 refreshment cycles, wastewater was deleted from the anolyte and only the nutrient solution was used for the subsequent acclimation and experiment cycles. During the entire study, the anolyte was normally refreshed every 2 days in order to sustain the unchangeable anode potential. The catholytes in MFCs_{Cr}, MFCs_{Cu} and MECs_{Cd} were 50 mg L⁻¹ Cr(VI), Cu(II) and Cd(II), respectively at a same initial pH of 2.0 in 100 mM NaCl solution (solution conductivity: 8.6 mS cm⁻¹). Prior to add the anolyte and catholyte in the system, the solutions were sparged with N₂ gas for 15 min. For acclimation of biofilms on all of the anodes, a same 100 mM NaCl solution (pH 2.0) with 50 mg L⁻¹ Cr(VI), Cu(II) and Cd(II) was used as the catholytes in MFCs_{Cr}, MFCs_{Cu} and MECs_{Cd}, respectively with each connected with an external resistor of 1000 Ω and individually developed at MFC mode [48]. After 7–8 cycle refreshments which totally lasted about 15–18 d, stable and repeatable anode potentials were observed in all MFCs_{Cr}, MFCs_{Cu} and MECs_{Cd}, implying the finish of anodic biofilms in these reactors. The established MFCs_{Cr} and MFCs_{Cu} were connected in series or parallel mode to drive MECs_{Cd} for simultaneous reduction of Cr(VI), Cu(II) and Cd(II) in this system, where CR was initially deliberately used as the cathodes of MECs_{Cd}, and then replaced by TS for efficient Cd(II) reduction consideration. A low resistance of 10 Ω was used in the circuit in order to measure

the circuit current although this including a resistor resulted in an additional voltage loss in the system and thus the actual applied voltage over the anode and cathode was smaller than the power source of MFCs_{Cr} and MFCs_{Cu}.

The performance of systems with different cathode empty bed volumes in MFCs (MFCs_{Cr} 25 mL – MFCs_{Cu} 25 mL, MFCs_{Cr} 13 mL – MFCs_{Cu} 25 mL, MFCs_{Cr} 25 mL – MFCs_{Cu} 13 mL, MFCs_{Cr} 13 mL – MFCs_{Cu} 13 mL) was deliberately explored whereas the volume in MECs_{Cd} was always 25 mL since a decrease in cathode volume in MECs negatively affected performance of MFC–MEC coupled system [34]. Together with considering stack MFCs_{Cr} and MFCs_{Cu}, MFCs_{Cr} 25 mL and MFCs_{Cu} 25 mL either in series or parallel connection was firstly assessed for system performance. Following this exploration, MFCs_{Cr} 13 mL – MFCs_{Cu} 25 mL in series (serial-Cr), MFCs_{Cr} 13 mL – MFCs_{Cu} 25 mL in parallel connection (parallel-Cr), MFCs_{Cr} 25 mL – MFCs_{Cu} 13 mL in series (serial-Cu), MFCs_{Cr} 25 mL – MFCs_{Cu} 13 mL in parallel connection (parallel-Cu), MFCs_{Cr} 13 mL – MFCs_{Cu} 13 mL in series (serial-both), and MFCs_{Cr} 13 mL – MFCs_{Cu} 13 mL in parallel connection (parallel-both) were extensively explored for enhanced system performance.

Three controls were also operated: one was run in open circuit mode to examine changes of Cr(VI), Cu(II) or Cd(II) in the absence of current generation. In the second control, MECs_{Cd} powered by individual MFCs_{Cr} or MFCs_{Cu} were explored to reflect the joint roles of MFCs_{Cr} and MFCs_{Cu} on MECs_{Cd}. In the third control, new bare cathodes with lacking Cr(VI), Cu(II) or Cd(II) in the catholyte were accordingly analyzed for redox behavior to exclude the roles of Cr(VI), Cu(II) or Cd(II) on electrode reactions. New cathodes were used for each operation cycle. All of the reactors were wrapped with aluminum foil to exclude light. All reactors were operated in fed-batch mode and all batch experiments were run in duplicate and maintained at room temperature (20 \pm 3 $^{\circ}$ C). All of the inoculation and solution replacements were performed in an anaerobic glove box (YQX-II, Xinmiao, Shanghai).

2.3. Measurements and analyses

Total chemical oxygen demand (COD) in the anolyte at an operation time of 4 h was measured using standard methods [49]. Ions of Cr(VI), Cu(II) and Cd(II) in the catholytes at the same operation time of 4 h were analyzed by an atomic absorption spectrophotometer (AAnalyst 700, PerkinElmer). Hydrogen produced in the headspaces of cathode chambers of MECs_{Cd} was analyzed using a gas chromatograph (GC7900, Tianmei, Shanghai) and a molecular sieve column (TDX-01, 60–80, 4 mm \times 2 m) with argon as the carrier gas. A scanning electronic microscopy (SEM) (QUANTA450, FEI company, USA) equipped with an energy dispersive X-ray spectrometer (EDS) (X-MAX 20 mm²/50 mm², Oxford Instruments, UK), and X-ray diffraction measurements (XRD-6000, Shimadzu LabX, Japan) were used to examine the morphologies of the electrodes before and after reduction of Cr(VI), Cu(II) and Cd(II), as well as the crystal products. The potentials of cathode and anode were collected by a data logger using an automatic data acquisition system (PISO-813, Hongge Co., Taiwan). Current density was normalized either to the cathode project area (A m⁻²) or to the cathode working volume (A m⁻³). The cathode redox behavior in MECs was studied using cyclic voltammetry (CV, CHI 650, Chenhua, Shanghai) at a scan rate of 1.0 mV s⁻¹. Linear sweep voltammetry (LSV) was performed using a potentiostat (CHI 650, Chenhua, Shanghai) at a scan rate of 0.1 mV s⁻¹. The three electrode system for both LSV and CV consisted of a working electrode (cathode electrode), counter electrode (platinum plate), and Ag/AgCl reference electrode (195 mV versus a standard hydrogen electrode, SHE). All potentials shown were corrected to a SHE.

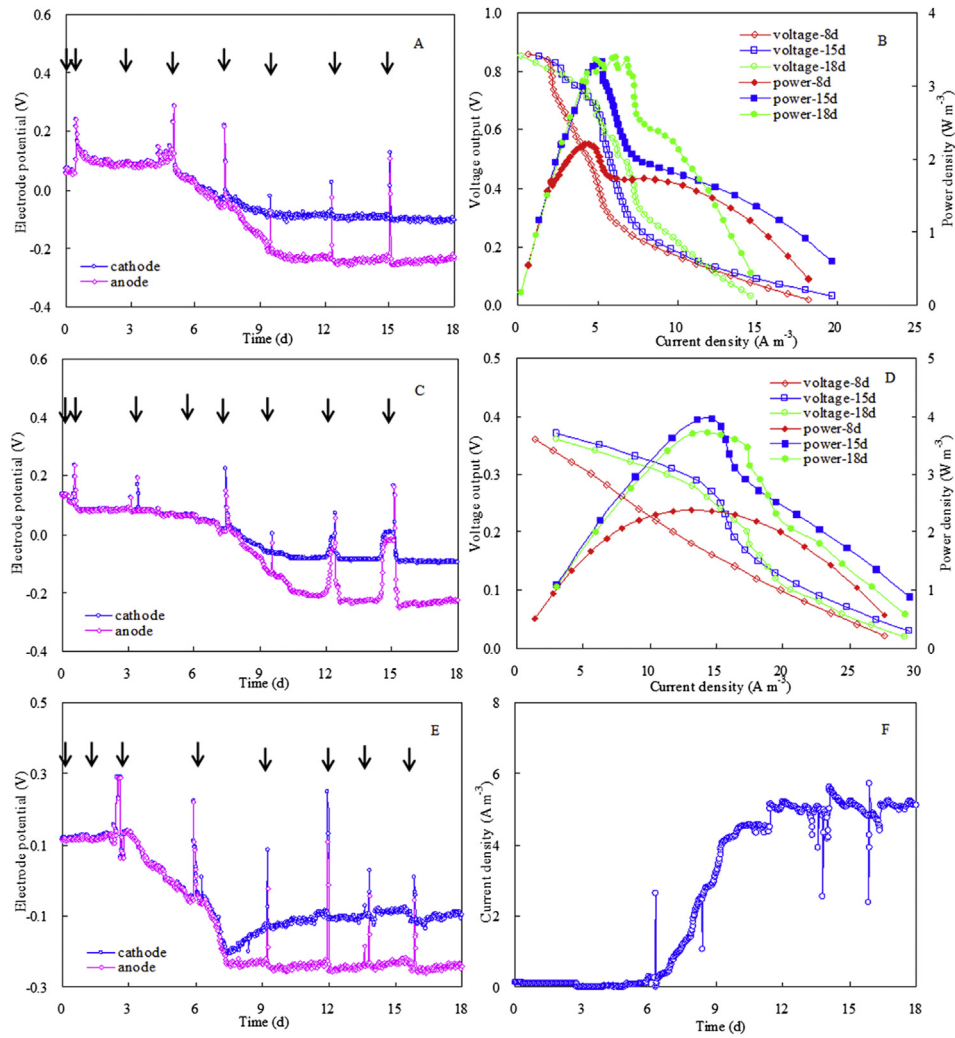


Fig. 1. Electrode potentials developed in individual (A) MFCs_{Cr}, (C) MFCs_{Cu} and (E) MECs_{Cd} at an external resistor of 1000 Ω . Polarization curves of (B) MFCs_{Cr} and (D) MFCs_{Cu} at various acclimation periods, and (F) circuit current in MECs_{Cd} (MFCs_{Cr}: 25 mL; MFCs_{Cu}: 25 mL; MECs_{Cd}: 25 mL; CR as the cathodes of MECs_{Cd}; arrows indicate when anodes and cathodes were fed with fresh medium).

2.4. Calculations

Cr(VI), Cu(II) and Cd(II) reduction was defined as the changes of Cr(VI), Cu(II) and Cd(II) concentrations at an operational period of 4 h divided by the initial Cr(VI), Cu(II) and Cd(II) concentrations in MFCs_{Cr}, MFCs_{Cu} and MECs_{Cd}, respectively (%). Hydrogen production ($\text{m}^3 \text{m}^{-3} \text{d}^{-1}$) in MECs_{Cd} was calculated based on hydrogen produced per cathode working volume per day. Yields of Cr (Y_{Cr} , mol Cr mol⁻¹ COD), Cu (Y_{Cu} , mol Cu mol⁻¹ COD) and Cd (Y_{Cd} , mol Cd mol⁻¹ COD), anodic coulombic efficiencies in terms of Cr (CE_{Cr} , %), Cu (CE_{Cu} , %), and Cd (CE_{Cd} , %), and cathodic coulombic efficiencies in terms of Cr (η_{Cr} , %), Cu (η_{Cu} , %) and Cd (η_{Cd} , %) were calculated, respectively as shown in Eqs. (4)–(13).

$$Y_{\text{Cr}} = \frac{\Delta C_{\text{Cr(VI)}} \times V_{\text{Cr,ca}} \times M_{\text{O}_2}}{\Delta \text{COD}_{\text{Cr}} \times V_{\text{an}} \times M_{\text{Cr}}} \quad (4)$$

$$Y_{\text{Cu}} = \frac{\Delta C_{\text{Cu(II)}} \times V_{\text{Cu,ca}} \times M_{\text{O}_2}}{\Delta \text{COD}_{\text{Cu}} \times V_{\text{an}} \times M_{\text{Cu}}} \quad (5)$$

$$Y_{\text{Cd}} = \frac{\Delta C_{\text{Cd(II)}} \times V_{\text{Cd,ca}} \times M_{\text{O}_2}}{\Delta \text{COD}_{\text{Cd}} \times V_{\text{an}} \times M_{\text{Cd}}} \quad (6)$$

$$\text{CE}_{\text{Cr}} = \frac{\int I dt}{96,485 \times \frac{4 \times \Delta \text{COD}_{\text{Cr}} \times V_{\text{an}}}{M_{\text{O}_2}}} \times 100\% \quad (7)$$

$$\text{CE}_{\text{Cu}} = \frac{\int I dt}{96,485 \times \frac{4 \times \Delta \text{COD}_{\text{Cu}} \times V_{\text{an}}}{M_{\text{O}_2}}} \times 100\% \quad (8)$$

$$\text{CE}_{\text{Cd}} = \frac{\int I dt}{96,485 \times \frac{4 \times \Delta \text{COD}_{\text{Cd}} \times V_{\text{an}}}{M_{\text{O}_2}}} \times 100\% \quad (9)$$

$$\eta_{\text{Cr}} = \frac{a_1 \times V_{\text{Cr,ca}} \times \Delta C_{\text{Cr(VI)}} \times 96,485}{M_{\text{Cr}} \times \int I dt} \times 100\% \quad (10)$$

$$\eta_{\text{Cu}} = \frac{a_2 \times V_{\text{Cu,ca}} \times \Delta C_{\text{Cu(II)}} \times 96,485}{M_{\text{Cu}} \times \int I dt} \times 100\% \quad (11)$$

$$\eta_{\text{Cd}} = \frac{a_3 \times V_{\text{Cd,ca}} \times \Delta C_{\text{Cd(II)}} \times 96,485}{M_{\text{Cd}} \times \int Idt} \times 100\% \quad (12)$$

$$\eta_{\text{sys}} = \frac{\Delta C_{\text{Cr(VI)}} \times V_{\text{Cr,ca}} \times \frac{a_1}{M_{\text{Cr}}} + \Delta C_{\text{Cu(II)}} \times V_{\text{Cu,ca}} \times \frac{a_2}{M_{\text{Cu}}} + \Delta C_{\text{Cd(II)}} \times V_{\text{Cd,ca}} \times \frac{a_3}{M_{\text{Cd}}}}{\left(V_{\text{an}} \Delta \text{COD}_{\text{Cr}} + V_{\text{an}} \Delta \text{COD}_{\text{Cu}} + V_{\text{an}} \Delta \text{COD}_{\text{Cd}} \right) \times \frac{4}{M_{\text{O}_2}}} \times 100\% \quad (13)$$

where $\Delta C_{\text{Cr(VI)}}$, $\Delta C_{\text{Cu(II)}}$ and $\Delta C_{\text{Cd(II)}}$ are the changes of Cr(VI), Cu(II) and Cd(II) concentrations in the catholytes of MFCs_{Cr}, MFCs_{Cu} and MECs_{Cd}, respectively at an operational period of 4 h (g L^{-1}); M_{Cr} , M_{Cu} and M_{Cd} are the atom weights of Cr, Cu and Cd, respectively (g mol^{-1}); V_{an} are identical anode working volumes of MFCs_{Cr}, MFCs_{Cu} and MECs_{Cd}, respectively (L); $V_{\text{Cr,ca}}$, $V_{\text{Cu,ca}}$ and $V_{\text{Cd,ca}}$ are cathode working volumes of MFCs_{Cr}, MFCs_{Cu} and MECs_{Cd}, respectively (L); $\Delta \text{COD}_{\text{Cr}}$, $\Delta \text{COD}_{\text{Cu}}$ and $\Delta \text{COD}_{\text{Cd}}$ are the cumulative COD values in the anolytes of MFCs_{Cr}, MFCs_{Cu} and MECs_{Cd}, respectively over an operational period of 4 h (g L^{-1}); I is circuit current (A); t is a set operational time (s); 96485 is Faraday constant ($\text{C mol}^{-1} \text{e}^{-}$); 4 is the molar number of electrons required for oxygen reduction (mol mol^{-1}); a_1 , a_2 and a_3 are the molar numbers of electrons required for Cr(VI), Cu(II) and Cd(II) reduction, respectively (mol mol^{-1}).

3. Results and discussion

3.1. Development of MFCs_{Cr}, MFCs_{Cu} and MECs_{Cd}

For each fed-batch cycle and with the prolonged acclimation period, the anode potentials in all MFCs_{Cr} (Fig. 1A), MFCs_{Cu} (Fig. 1C) and MECs_{Cd} (Fig. 1E) gradually became more negative whereas cathode potentials in these reactors were always sustained at $-0.094 \sim -0.098$ V, reflecting the development of biofilms on these anodes. After a 15-day acclimation period, anode potentials were stably and repeatedly sustained at $-0.23 \sim -0.27$ V, a value generally achieved using acetate as a fuel in MFCs [5]. These results demonstrate the finish of bioanode acclimation for all MFCs_{Cr}, MFCs_{Cu} and MECs_{Cd}. The maximum power obtained from polarization data clearly showed the changes in voltage output and power production from both MFCs_{Cr} (Fig. 1B) and MFCs_{Cu} (Fig. 1D) with the acclimation period. At an acclimation time of 15 d, MFCs_{Cr} and MFCs_{Cu} exhibited maximal powers of 3.3 W m^{-3} (5.1 A m^{-3}) (Fig. 1B) and 4.0 W m^{-3} (14.7 A m^{-3}) (Fig. 1D), respectively, both of which were similar to those at an acclimation time of 18 d. These results demonstrate the necessary acclimation period of 15 d for both MFCs_{Cr} and MFCs_{Cu}. The higher open circuit potential in MFCs_{Cr} (Fig. 1B) than that in MFCs_{Cu} (Fig. 1D) was mainly ascribed to the much higher cathode theoretical potential of 1.02 V for half-reaction of Cr(VI) to Cr(III) in MFCs_{Cr} than 0.25 V for Cu(II) to Cu in MFCs_{Cu} under the present experimental condition. Accordingly, reduction of Cr(VI) in MFCs_{Cr} and Cu(II) in MFCs_{Cu} also experienced gradual increase, achieving 34.2% and 25.4%, reduction rates of $4.28 \text{ mg L}^{-1} \text{h}^{-1}$ and $3.18 \text{ mg L}^{-1} \text{h}^{-1}$, respectively at a same acclimation period of 15–18 d, demonstrating that power production was directly relative to Cr(VI) and Cu(II) reduction. This Cu(II) reduction rate was in the range of reported $1.29 \sim 29 \text{ mg L}^{-1} \text{h}^{-1}$ at initial Cu(II) concentrations of $100 \sim 6400 \text{ mg L}^{-1}$ and pHs of 2.0–4.7 [13–17] whereas Cr(VI) reduction rate was higher than the previous $0.14 \sim 0.67 \text{ mg L}^{-1} \text{h}^{-1}$ at initial Cr(VI) concentrations of $39 \sim 100 \text{ mg L}^{-1}$ and pHs of 2.0–7.0 in H-type MFCs [10,11]. Similarly

and in the case of MECs_{Cd}, after an acclimation time of 15 d, there were no apparent changes in both electrode potential (Fig. 1E) and circuit current (Fig. 1F) with an achievement of Cd(II) reduction of 11.7% ($1.46 \text{ mg L}^{-1} \text{h}^{-1}$), implying again the finish of MECs_{Cd}

acclimation. The MECs_{Cd} was then connected and self-driven by MFCs_{Cr} and MFCs_{Cu} in series or parallel connection for the subsequent operation.

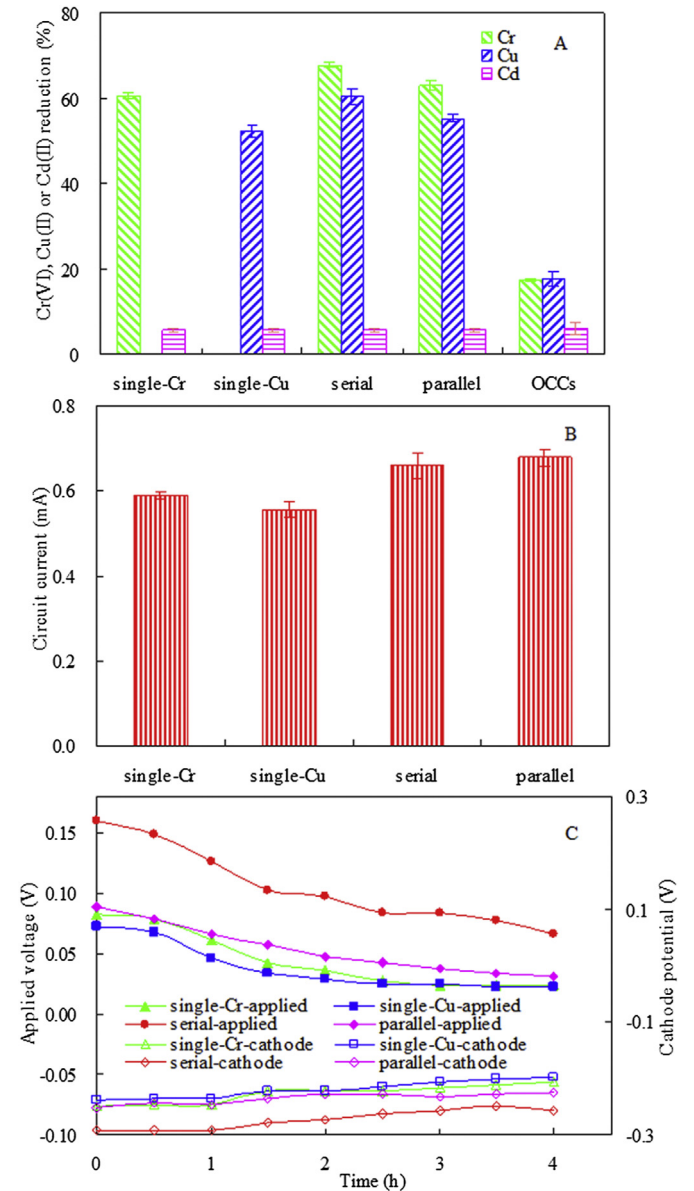


Fig. 2. (A) Reduction of Cr(VI) in MFCs_{Cr}, Cu(II) in MFCs_{Cu} and Cd(II) in MECs_{Cd}, (B) circuit current, and (C) applied voltage and cathode potential in MECs_{Cd} (single-Cr: single MFCs_{Cr} 25 mL; single-Cu: single MFCs_{Cu} 25 mL; serial: MFCs_{Cr} 25 mL and MFCs_{Cu} 25 mL serially connected; parallel: MFCs_{Cr} 25 mL and MFCs_{Cu} 25 mL in parallel connection; CR as the cathodes of MECs_{Cd}).

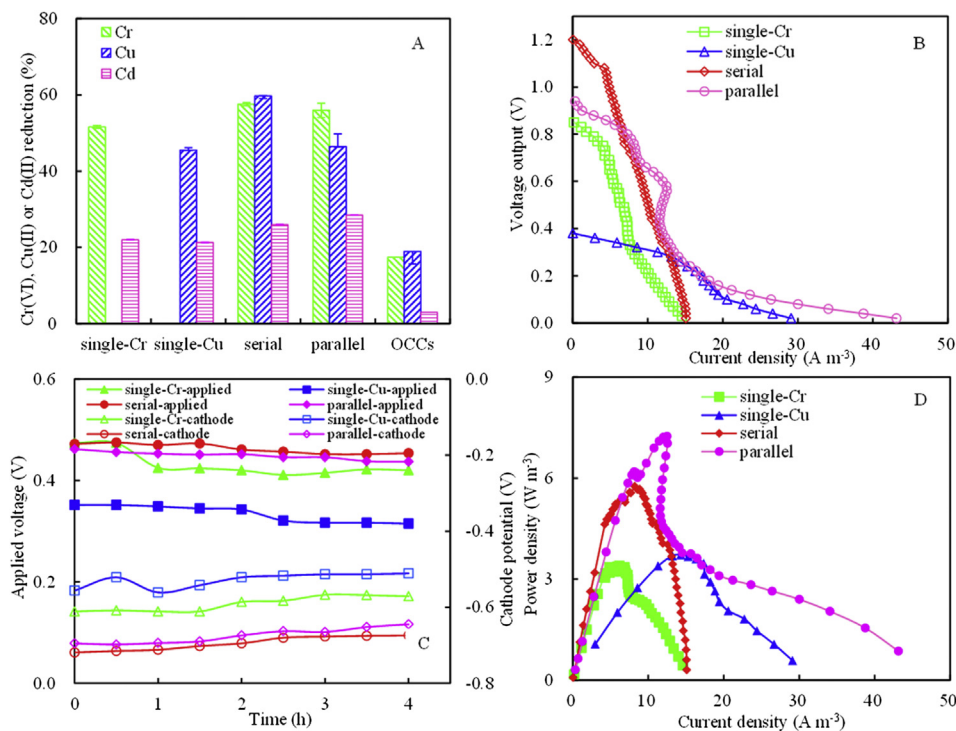


Fig. 3. (A) Reduction of Cr(VI) in MFCs_{Cr}, Cu(II) in MFCs_{Cu} and Cd(II) in MECs_{Cd}, (B) relationship of voltage output and current density in single MFCs_{Cr}, single MFCs_{Cu}, or both in a stack, (C) applied voltage and cathode potential in MECs_{Cd}, and (D) relationship of power production and current density in single MFCs_{Cr}, single MFCs_{Cu}, or both stacked (single-Cr: single MFCs_{Cr} 25 mL; single-Cu: single MFCs_{Cu} 25 mL; serial: MFCs_{Cr} 25 mL and MFCs_{Cu} 25 mL serially connected; parallel: MFCs_{Cr} 25 mL and MFCs_{Cu} 25 mL in parallel connection; TS as the cathodes of MECs_{Cd}).

3.2. CR cathodes of MECs_{Cd}

Under a serial configuration, reduction of Cr(VI) in MFCs_{Cr} ($67.6 \pm 0.5\%$) and Cu(II) in MFCs_{Cu} ($60.4 \pm 2.1\%$) was somewhat higher than $62.9 \pm 1.1\%$ and $55.3 \pm 1.0\%$, respectively with parallel connection (Fig. 2A). While a circuit current of 0.66 ± 0.03 mA in series approached 0.68 ± 0.02 mA in parallel connection (Fig. 2B), individual MFCs_{Cr} or MFCs_{Cu} actually shared this entire circuit current in parallel connection compared to the identical value in serial MFCs_{Cr} and MFCs_{Cu}, explaining the more efficient Cr(VI) and Cu(II) reduction in the latter (Fig. 2A). Cr(VI) reduction ($60.5 \pm 0.6\%$) in individual MFCs_{Cr} driving MECs_{Cd} system and

Cu(II) reduction ($52.4 \pm 1.5\%$) in single MFCs_{Cu} driving MECs_{Cd} system were lower than those in stack MFCs_{Cr} and MFCs_{Cu} (Fig. 2A), also attributable to the lower circuit current in the former (Fig. 2B) and reflecting the beneficial stack MFCs_{Cr} and MFCs_{Cu} for Cr(VI) and Cu(II) reduction. While voltage reversal occurred during MFC stack operation and adversely affected power output [50], the majority of the cells performing well can compensate for the negative effects of the underperforming minority [42], explaining the positive effects of stack MFCs_{Cr} and MFCs_{Cu} on Cr(VI) and Cu(II) reduction inside. In the OCC controls, only a similar 17.7% of Cr(VI) and Cu(II) was removed (Fig. 2A), mainly attributable to chemical adsorption on the CR cathodes

Table 1
Yields of chromium, copper and cadmium, hydrogen production and operational efficiencies in MFCs_{Cr}–MFCs_{Cu}–MECs_{Cd} system under various working volumes in cathodes of MFCs_{Cr} and/or MFCs_{Cu} with different connections (TS as cathodes of MECs_{Cd}).

| MFCs _{Cr} – MFCs _{Cu} | Parameters | Yield | | | Hydrogen production (m ³ m ⁻³ d ⁻¹) | CE | | | η | | | $\eta_{\text{sys}} (\%)$ |
|--|---------------|--|--|--|---|----------------------|----------------------|----------------------|-------------------------|-------------------------|-------------------------|--------------------------|
| | | $Y_{\text{Cr}} (\text{mol Cr mol}^{-1} \text{ COD})$ | $Y_{\text{Cu}} (\text{mol Cu mol}^{-1} \text{ COD})$ | $Y_{\text{Cd}} (\text{mol Cd mol}^{-1} \text{ COD})$ | | CE _{Cr} (%) | CE _{Cu} (%) | CE _{Cd} (%) | $\eta_{\text{Cr}} (\%)$ | $\eta_{\text{Cu}} (\%)$ | $\eta_{\text{Cd}} (\%)$ | |
| 25–0 | Single-Cr | 0.52 ± 0.00 | — | 0.09 ± 0.01 | 0.0023 ± 0.0001 | 55 ± 0 | — | 48 ± 0 | 69 ± 1 | — | 9 ± 1 | 24 ± 0 |
| 0–25 | Single-Cu | — | 0.57 ± 0.04 | 0.13 ± 0.03 | 0.0018 ± 0.0000 | — | 43 ± 2 | 49 ± 2 | — | 54 ± 1 | 13 ± 2 | 20 ± 0 |
| 25–25 | Serial | 0.47 ± 0.00 | 0.42 ± 0.03 | 0.09 ± 0.02 | 0.0166 ± 0.0021 | 65 ± 1 | 69 ± 1 | 66 ± 1 | 47 ± 0 | 27 ± 1 | 7 ± 0 | 22 ± 0 |
| 25–25 | Parallel | 0.54 ± 0.00 | 0.25 ± 0.09 | 0.12 ± 0.04 | 0.0307 ± 0.0002 | 79 ± 4 | 76 ± 3 | 77 ± 4 | 49 ± 2 | 19 ± 4 | 7 ± 0 | 24 ± 1 |
| 13–0 | Single-Cr | 0.36 ± 0.02 | — | 0.18 ± 0.00 | 0.0017 ± 0.0001 | 42 ± 4 | — | 38 ± 4 | 66 ± 4 | — | 27 ± 4 | 21 ± 1 |
| 0–13 | Single-Cu | — | 0.38 ± 0.03 | 0.14 ± 0.05 | 0.0014 ± 0.0001 | — | 24 ± 0 | 25 ± 0 | — | 65 ± 0 | 27 ± 5 | 14 ± 3 |
| 13–25 | Serial-Cr | 0.27 ± 0.03 | 0.40 ± 0.05 | 0.23 ± 0.04 | 0.0022 ± 0.0001 | 54 ± 1 | 52 ± 1 | 53 ± 1 | 34 ± 1 | 34 ± 4 | 10 ± 1 | 17 ± 1 |
| 25–13 | Serial-Cu | 0.41 ± 0.02 | 0.21 ± 0.01 | 0.21 ± 0.03 | 0.0020 ± 0.0001 | 47 ± 7 | 45 ± 7 | 46 ± 7 | 63 ± 8 | 22 ± 4 | 13 ± 2 | 18 ± 0 |
| 13–25 | Parallel-Cr | 0.27 ± 0.03 | 0.26 ± 0.04 | 0.18 ± 0.02 | 0.0040 ± 0.0004 | 46 ± 1 | 47 ± 1 | 45 ± 1 | 40 ± 1 | 28 ± 2 | 8 ± 1 | 15 ± 1 |
| 25–13 | Parallel-Cu | 0.31 ± 0.03 | 0.21 ± 0.03 | 0.19 ± 0.03 | 0.0022 ± 0.0002 | 44 ± 1 | 43 ± 1 | 42 ± 1 | 46 ± 6 | 22 ± 4 | 15 ± 2 | 15 ± 0 |
| 13–13 | Serial-both | 0.32 ± 0.01 | 0.21 ± 0.04 | 0.19 ± 0.04 | 0.0041 ± 0.0002 | 33 ± 1 | 31 ± 1 | 38 ± 1 | 67 ± 2 | 39 ± 0 | 10 ± 1 | 17 ± 0 |
| 13–13 | Parallel-both | 0.24 ± 0.04 | 0.22 ± 0.03 | 0.20 ± 0.03 | 0.0048 ± 0.0009 | 36 ± 3 | 35 ± 3 | 34 ± 3 | 46 ± 2 | 33 ± 2 | 13 ± 1 | 15 ± 1 |

Note: single-Cr: single MFCs_{Cr} with 25 mL or 13 mL; single-Cu: single MFCs_{Cu} with 25 mL or 13 mL; serial: MFCs_{Cr} 25 mL – MFCs_{Cu} 25 mL in serial; parallel: MFCs_{Cr} 25 mL – MFCs_{Cu} 25 mL in parallel; serial-Cr: MFCs_{Cr} 13 mL – MFCs_{Cu} 25 mL in serial; parallel-Cr: MFCs_{Cr} 13 mL – MFCs_{Cu} 25 mL in parallel; serial-Cu: MFCs_{Cr} 25 mL – MFCs_{Cu} 13 mL in serial; parallel-Cu: MFCs_{Cr} 25 mL – MFCs_{Cu} 13 mL in parallel; serial-both: MFCs_{Cr} 13 mL – MFCs_{Cu} 13 mL in serial; parallel-both: MFCs_{Cr} 13 mL – MFCs_{Cu} 13 mL in parallel.

and reflecting the importance of circuit current on Cr(VI) and Cu(II) reduction in this system.

Different from reduction of Cr(VI) in MFCs_{Cr} and Cu(II) in MFCs_{Cu}, Cd(II) reduction in all of the MECs_{Cd} (driven by serial MFCs_{Cr} and MFCs_{Cu}, parallel MFCs_{Cr} and MFCs_{Cu}, individual MFCs_{Cr} or MFCs_{Cu}, as well as OCC controls) was similarly as low as 5.6–6.1% (Fig. 2A), demonstrating no occurrence of Cd(II) reduction on the CR cathodes of MECs_{Cd} whatever MFCs_{Cr} and MFCs_{Cu} were stacked. This result can be explained by the similarly low applied voltages and high cathode potentials in MECs_{Cd} (Fig. 2C), both of which were below the minimal requirements for the half reaction of Cd(II) reduction (Eq. (3)).

3.3. TS cathodes of MECs_{Cd}

TS was deliberately used as the cathodes of MECs_{Cd} to explore efficient Cd(II) reduction with simultaneous Cr(VI) and Cu(II) reduction in this self-driven system. A highest Cd(II) reduction of $28.5 \pm 0.02\%$ (Fig. 3A) concomitant with a highest hydrogen production of $0.0307 \pm 0.0002 \text{ m}^3 \text{ m}^{-3} \text{ d}^{-1}$ (Table 1) was achieved in MECs_{Cd} self-driven by MFCs_{Cr} and MFCs_{Cu} in parallel connection, followed by $25.9 \pm 0.04\%$ (Cd(II) reduction) (Fig. 3A) and $0.0166 \pm 0.0021 \text{ m}^3 \text{ m}^{-3} \text{ d}^{-1}$ (hydrogen production) (Table 1) in serially connected system. The stack MFCs_{Cr} and MFCs_{Cu} either in series or parallel connection exhibited higher voltage output (Fig. 3B) and power production (Fig. 3D) than those in single MFCs_{Cr} or MFCs_{Cu} controls. While MFCs_{Cr} and MFCs_{Cu} in series had an open circuit potential of 1.20 V, reasonably higher than 0.94 V in parallel connection and a little bit lower than the sum of 1.23 V of single MFCs_{Cr} and MFCs_{Cu} (Fig. 3B), the unavoidable occurrence of more severe voltage reversal [18,19] in serially connected MFCs_{Cr} and MFCs_{Cu} may have resulted in similar applied voltages and cathode potentials in MECs_{Cd} to those in parallel connection (Fig. 3C). MECs_{Cd} driven by either single MFCs_{Cr} or MFCs_{Cu} had a similar Cd(II) reduction of $21.6 \pm 0.8\%$ (Fig. 3A), lower than the $25.9 \pm 0.04\%$ – $28.5 \pm 0.02\%$ in stack MFCs_{Cr} and MFCs_{Cu}, and substantially higher than that in the OCC controls ($3.0 \pm 0.1\%$ with TS cathodes (Fig. 3A), 5.6–6.0% with CR cathodes (Fig. 2A)). These results demonstrate the preferable stack MFCs_{Cr} and MFCs_{Cu} for Cd(II) reduction in the connected MECs_{Cd}, and the importance of both TS cathodes of MECs_{Cd} and circuit current on efficient Cd(II) reduction inside. It is commonly understood higher applied voltages decreased cathode potentials of MECs_{Cd}, and thus promoted Cd(II) reduction (Eq. (3)). In fact, a more negative cathode potential created a more reduced environment [14,15], which was more favorable for electrons to transfer from the cathodes to reduce Cd(II) in MECs_{Cd}.

Reduction of Cr(VI) in MFCs_{Cr} and Cu(II) in MFCs_{Cu} (Fig. 3A) under either serial or parallel connection exhibited somewhat lower than that with CR cathodes of MECs_{Cd} under the same stack MFCs_{Cr} and MFCs_{Cu} (Fig. 2A), mainly ascribed to the more electrons shared by Cd(II) reduction in the former (Fig. 3A) compared to no electrons consumption for Cd(II) reduction in the latter (Fig. 2A). Similarly, Cr(VI) ($60.5 \pm 0.6\%$) and Cu(II) ($52.4 \pm 1.5\%$) reduction in single reactors (Fig. 3A) was also lower than those with CR cathodes of MECs_{Cd} (Fig. 2A). These results reflect the competitive Cr(VI), Cu(II) and Cd(II) reduction for circuit electrons, and stress the critical role of TS cathodes of MECs_{Cd} in simultaneous reduction of Cd(II) in MECs_{Cd}, Cr(VI) in MFCs_{Cr} and Cu(II) in MFCs_{Cu}.

In terms of product yield and compared to individual MFCs_{Cr} or MFCs_{Cu} driving MECs_{Cd} controls, MFCs_{Cr} and MFCs_{Cu} in either parallel or serial connection was apparently unfavorable for Y_{Cu} in spite of a slightly high Y_{Cr} at parallel connection (Table 1). MFCs_{Cr} and MFCs_{Cu} in parallel connection had a similar Y_{Cd} to single MFCs_{Cu} driving MECs_{Cd} system. In addition, MFCs_{Cr} and MFCs_{Cu}

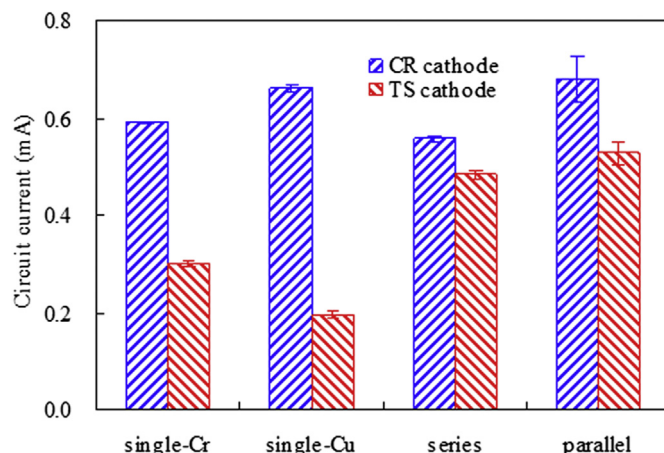


Fig. 4. Circuit current using either CR or TS as the cathodes of MECs_{Cd} (single-Cr: single MFCs_{Cr} 25 mL; single-Cu: single MFCs_{Cu} 25 mL; serial: MFCs_{Cr} 25 mL and MFCs_{Cu} 25 mL serially connected; parallel: MFCs_{Cr} 25 mL and MFCs_{Cu} 25 mL in parallel connection).

serially stacked exhibited an identical Y_{Cd} with single MFCs_{Cr} driving MECs_{Cd} system (Table 1). These results imply no appreciable benefits from the different stack MFCs_{Cr} and MFCs_{Cu} to all yields of Y_{Cr}, Y_{Cu} and Y_{Cd}. In terms of anodic CEs, MFCs_{Cr} and MFCs_{Cu} in parallel connection was superior to the serial stack, both of which were substantially higher than the individual MFCs_{Cr} or MFCs_{Cu} driving MECs_{Cd} system (Table 1). In any cases mentioned above, CE_{Cu} was always much higher than the 2% previously reported in single MFCs_{Cu} [15], implying the more efficiency of the anodes of MFCs_{Cu} to extract electrons from organics. MFCs_{Cr} and MFCs_{Cu} in either serial or parallel connection were detrimental to cathodic CEs of η_{Cr} , η_{Cu} and η_{Cd} whereas system efficiency always averaged $22.5 \pm 1.9\%$ (Table 1). These results demonstrate the bilateral effects of stack MFCs_{Cr} and MFCs_{Cu} on these parameters aforementioned.

3.4. Comparison of circuit current under CR and TS cathodes of MECs_{Cd}

Electron supply is affected by current generation, and a higher circuit current or a flow of more electrons will benefit to metal reduction on the cathodes [7]. CR cathodes of MECs_{Cd} generally had a higher circuit current than TS cathodes, reaching $0.59 \pm 0.003 \text{ mA}$ (single MFCs_{Cr}) and $0.66 \pm 0.01 \text{ mA}$ (single MFCs_{Cu}) compared to

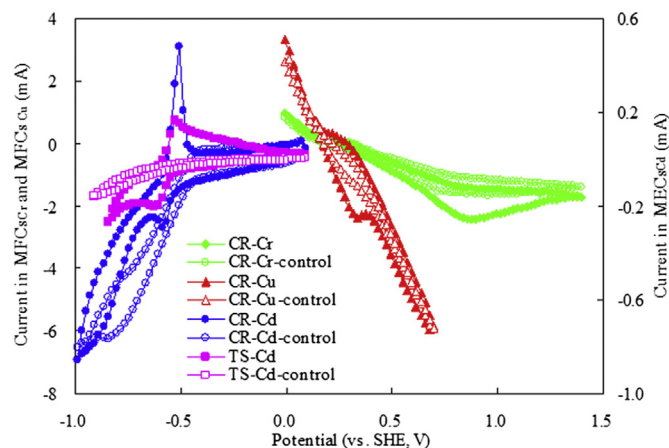


Fig. 5. Comparison of CV tests carried out on the CR cathodes of MFCs_{Cr}, MFCs_{Cu} and MECs_{Cd}, as well as the TS cathodes of MECs_{Cd} with the presence/absence of Cr(VI), Cu(II) or Cd(II), respectively.

0.30 ± 0.01 mA (single MFCs_{Cr}) and 0.19 ± 0.01 mA (single MFCs_{Cu}) in the latter (Fig. 4). A lower resistance of CR than TS [39,51] as the cathodes of MECs_{Cd} understandably decreased the resistance of the entire MECs_{Cd} , which was equivalent to the external resistance of the connected MFCs_{Cr} and MFCs_{Cu} , and thus led to a higher circuit current (Fig. 4). This higher circuit current explains the more efficient reduction of Cr(VI) in MFCs_{Cr} and Cu(II) in MFCs_{Cu} , either of which can drive MECs_{Cd} with CR cathodes (Fig. 2A). Besides the beneficial high circuit current for Cr(VI) and Cu(II) reduction on the cathodes, a low enough cathode potential was also essential for proceeding the corresponding reactions [7]. Compared to the lower resistance of CR, TS as the cathodes of MECs_{Cd} had apparently decreased the electrode potential low enough for proceeding Cd(II) reduction in MECs_{Cd} self-driven by MFCs_{Cr} and/or MFCs_{Cu} (Fig. 3C) in spite of a somewhat decrease in circuit current (Fig. 4). These results illustrate the importance of cathode potential of MECs_{Cd} and circuit current, both of which were essential for efficient Cd(II) reduction with simultaneous Cr(VI) and Cu(II) reduction in this system.

3.5. Cyclic voltammetry tests

Reduction of Cr(VI) on the CR cathodes of MFCs_{Cr} , Cu(II) on the CR cathodes of MFCs_{Cu} , and Cd(II) on both the CR and TS cathodes of MECs_{Cd} were further assessed using CV. Apparent reduction peaks of 0.86 V for Cr(VI) and 0.34 V for Cu(II) were observed, with no peaks measured in the controls with the absence of Cr(VI) and Cu(II), respectively (Fig. 5), consistent with the half reactions shown in Eqs. (1), (2). In contrast, one similar reduction peak of -0.62 V appeared on both the CR and TS cathodes with the presence of Cd(II), more negative than those of Cr(VI) and Cu(II), and in agreement with the half reaction in Eq. (3). These results show that substrate species had a substantial impact on the potentials of the oxidation-reduction peaks. The sizes of oxidation-reduction peaks were significantly different with similar maximums for Cr(VI) and Cu(II) on the CR cathodes, and minimum for Cd(II) on both the CR and TS cathodes (Fig. 5). Compared to TS cathodes, the larger size of oxidation-reduction peaks on the CR cathodes with the presence of Cd(II) ions indicates the more

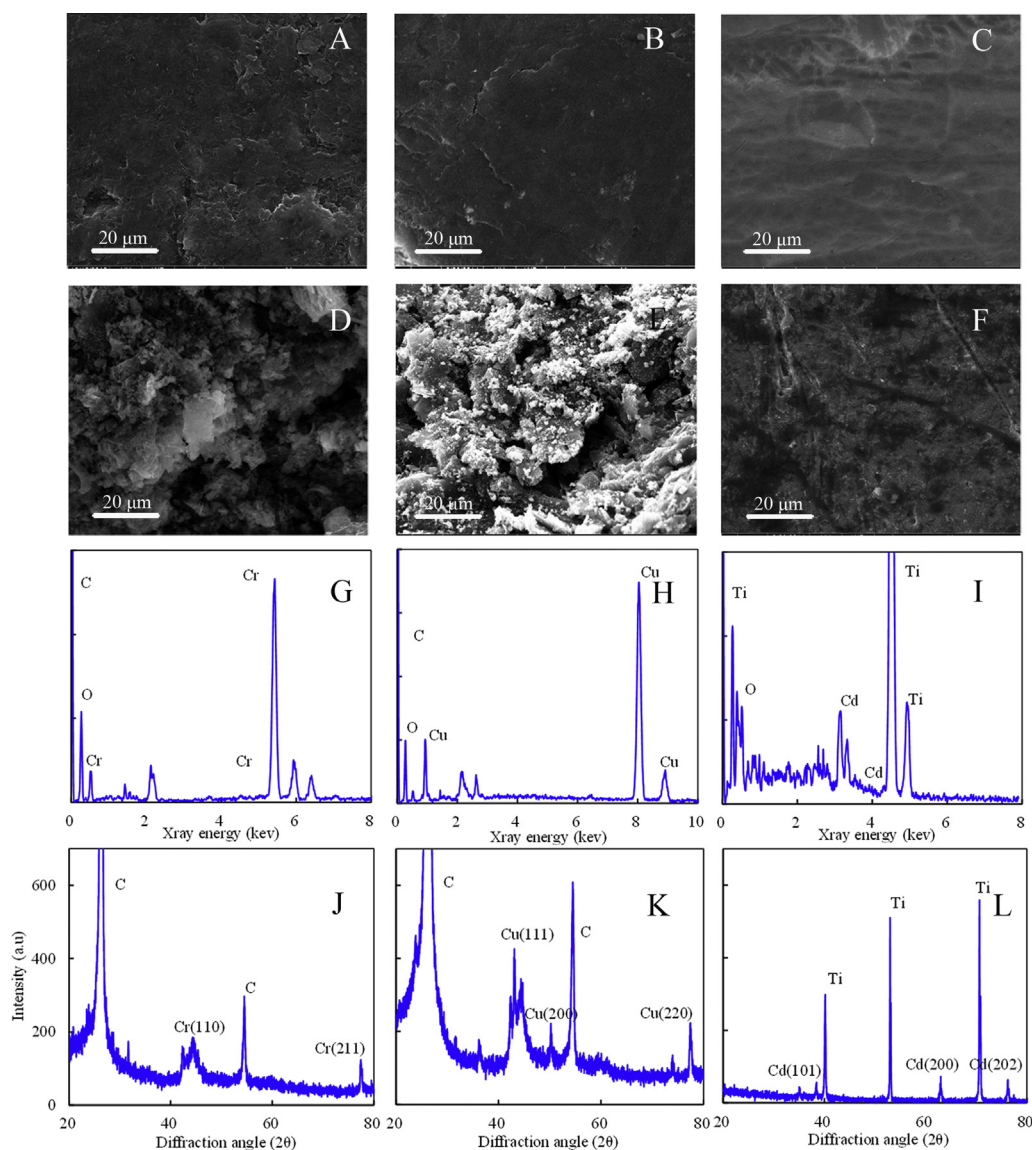


Fig. 6. SEM observations on the cathodes of MFCs_{Cr} (A and D), MFCs_{Cu} (B and E) and MECs_{Cd} (C and F) before (A, B and C) and after (D, E and F) Cr(VI), Cu(II) and Cd(II) reduction, respectively. EDS (G, H and I) and XRD (J, K and L) analyses on products of Cr(VI) (G and J), Cu(II) (H and K) and Cd(II) (I and L) reduction.

conductivity, more efficient surface area and/or more electro-catalytic activities of the CR electrodes.

3.6. Morphologies of electrodes and product analysis

SEM images clearly showed distinctive structure and morphology (Fig. 6). The cathodic surfaces in MFCs_{Cr} and MFCs_{Cu} were densely and evenly covered by a layer of spherule shape crystals after Cr(VI) and Cu(II) reduction (Fig. 6D and E), compared to the bare electrodes, respectively (Fig. 6A and B). Differently, a smooth layer was observed on the cathodes from Cd(II) ion solution (Fig. 6F) in comparison with the bare electrodes (Fig. 6C). Using EDS to examine the composition of the precipitates, Cr, Cu and Cd signals were detected on the precipitates of MFCs_{Cr} (Fig. 6G), MFCs_{Cu} (Fig. 6H) and MECs_{Cd} (Fig. 6I) electrodes, respectively. XRD spectra showed chromium peaks were clearly present in the spectrum for powder collected from the MFCs_{Cr} cathodes with a stronger Cr (110) relative peak intensity at 44.8° than Cr (211) at 77.5° (Fig. 6J). Similarly, a stronger Cu (111) relative peak intensity at 43.2° than others of Cu (200) at 50.4° and Cu (220) at 74.1° (Fig. 6K) whereas similarly weak cadmium peaks of Cd (101) at 36.0°, Cd (200) at 63.1° and Cd (202) at 76.2° were observed (Fig. 6L).

The products formed on the cathodes were mainly dependent on substrate concentration and pH value [14,15]. Under the experimental temperature of 20 ± 3 °C and an identical Cr(VI), Cu(II) or Cd(II) concentration of 50 mg L⁻¹, cathode theoretical potentials of the three reactions (Eqs. (1)–(3)) at different pHs were calculated based on the Nernst equations similar as the reported [14,15] and shown in Fig. 7. Considering the final pHs of 3.5–4.1 in MFCs_{Cr}, 2.4–3.7 in MFCs_{Cu} and 2.3–4.1 in MECs_{Cd}, species of Cr(VI) in MFCs_{Cr}, Cu(II) in MFCs_{Cu} and Cd(II) in MECs_{Cd} were reductively changed to Cr(OH)₃ (Fig. 7A), pure copper (Fig. 7B) and pure cadmium (Fig. 7C), respectively under the present experimental conditions, confirming the final products in this system (Fig. 6).

3.7. Various cathode volumes in stack MFCs_{Cr} and MFCs_{Cu}

A decrease in cathode volume in either MFCs_{Cr} or MFCs_{Cu} and serially connected with volume-unchanged MFCs_{Cu} or MFCs_{Cr} improved Cd(II) reduction in MECs_{Cd}, achieving $41.4 \pm 2.2\%$ for MFCs_{Cr} 13 mL – MFCs_{Cu} 25 mL in series (serial-Cr) and $38.4 \pm 3.3\%$ for serially connected MFCs_{Cr} 25 mL – MFCs_{Cu} 13 mL (serial-Cu) (Fig. 8A), improvements of 59.8% and 48.3%, respectively compared to the $25.9 \pm 0.04\%$ for serially connected and volume-unchanged MFCs_{Cr} 25 mL – MFCs_{Cu} 25 mL (Fig. 3A). In terms of product yields, anodic CEs and cathodic CEs, serial connection in most cases was superior to the corresponding parallel connection whereas hydrogen production in parallel connection was higher than those in series (Table 1). Higher cadmium yields of 0.23 ± 0.04 mol Cd mol⁻¹ COD in serial-Cr and 0.21 ± 0.03 mol Cd mol⁻¹ COD in serial-Cu were reasonably obtained (Table 1). Accordingly, amounting to $56.4 \pm 0.5\%$ of Cr(VI) and $52.7 \pm 3.5\%$ of Cu(II) in serial-Cr, and $45.8 \pm 0.5\%$ of Cr(VI) and $62.1 \pm 0.5\%$ of Cu(II) in serial-Cu were reduced (Fig. 8A) with product yields of 0.27 ± 0.03 mol Cr mol⁻¹ COD and 0.40 ± 0.05 mol Cu mol⁻¹ COD in the former, and 0.41 ± 0.02 mol Cr mol⁻¹ COD and 0.21 ± 0.01 mol Cu mol⁻¹ COD in the latter (Table 1). These results were mainly attributable to the similarly high circuit current of 0.36 ± 0.02 mA (Fig. 8B), and high applied voltages of 0.40–0.44 V (Fig. 8E) as well as low cathode potentials of $-0.66 \sim -0.72$ V in MECs_{Cd} (Fig. 8F), all of which were resulted from high voltage output (Fig. 8C) and current output (Fig. 8D) from either serial-Cr or serial-Cu system.

In terms of Cr(VI) and Cu(II) reduction, a decrease in cathode volume in both MFCs_{Cr} and MFCs_{Cu}, and serially connected each

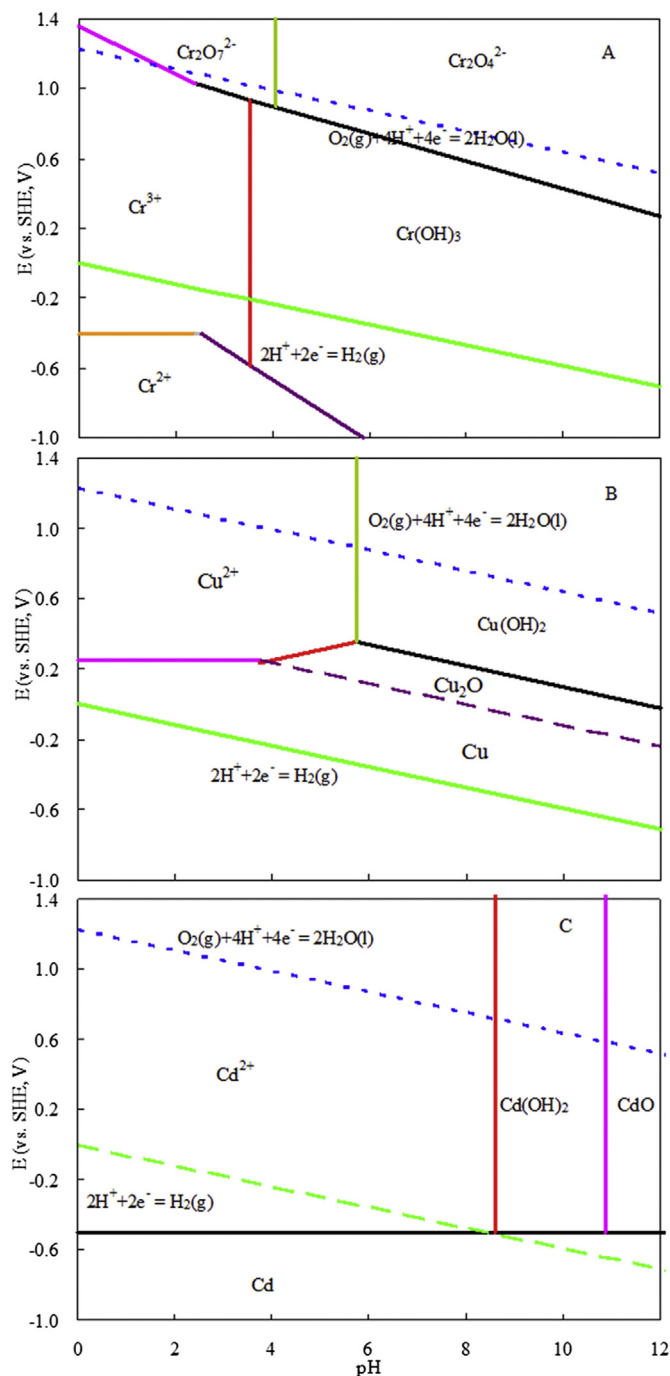


Fig. 7. Cathode theoretical potentials for half-reactions of (A) Cr(VI) to Cr(III) in MFCs_{Cr}, (B) Cu(II) to Cu in MFCs_{Cu}, and (C) Cd(II) to Cd in MECs_{Cd} at different pH values.

other (MFCs_{Cr} 13 mL – MFCs_{Cu} 13 mL in series; serial-both) was the most beneficial, exhibiting Cr(VI) reduction of $63.5 \pm 0.5\%$ and Cu(II) reduction of $68.8 \pm 1.1\%$, respectively (Fig. 8A), compared to 57.6% (Cr(VI) reduction) and 59.7% (Cu(II) reduction) in volume-unchanged MFCs_{Cr} 25 mL – MFCs_{Cu} 25 mL in series (Fig. 3A). However, only $27.8 \pm 2.2\%$ of Cd(II) was reduced in serial-both, similar to $31.2 \pm 1.5\%$ in parallel-both (Fig. 8A), reflecting no appreciable Cd(II) reduction in MECs_{Cd} self-driven by MFCs_{Cr} and MFCs_{Cu} with a decrease in cathode volume in both and in series or parallel connection.

In the controls of individual MFCs_{Cu} driving MECs_{Cd} system, amounting to $56.7 \pm 0.1\%$ of Cu(II) was reduced on the half-volume

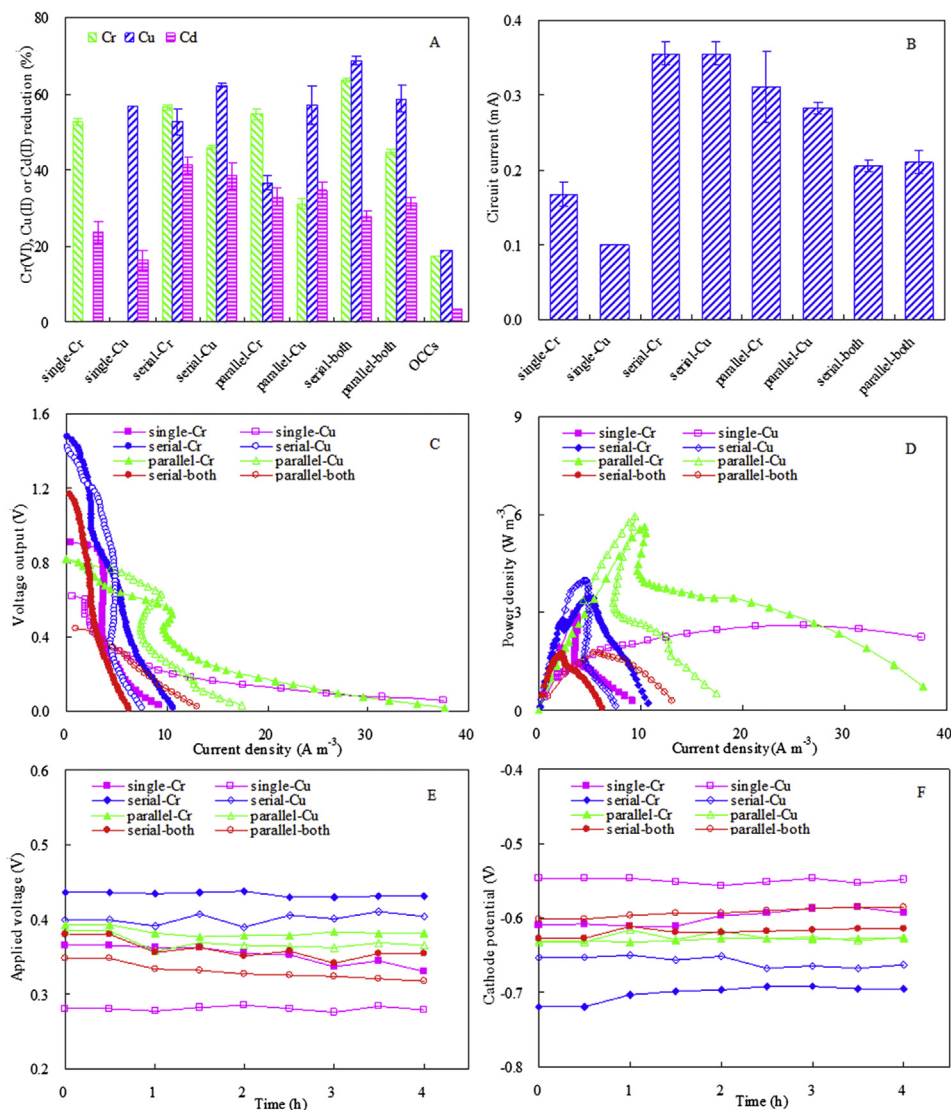


Fig. 8. (A) Reduction of Cr(VI) in MFCsCr, Cu(II) in MFCsCu and Cd(II) in MECsCd, (B) circuit current, (C) voltage output and (D) power production from MFCsCr and/or MFCsCu, (E) applied voltage in MECsCd, and (F) cathode potential of MECsCd under various cathode volumes in stack MFCsCr and MFCsCu (single-Cr: single MFCsCr, 13 mL; single-Cu: single MFCsCu, 13 mL; serial-Cr: MFCsCr 13 mL – MFCsCu 25 mL in series; parallel-Cr: MFCsCr 13 mL – MFCsCu 25 mL in parallel connection; serial-Cu: MFCsCr 25 mL – MFCsCu 13 mL in series; parallel-Cu: MFCsCr 25 mL – MFCsCu 13 mL in parallel connection; serial-both: MFCsCr 13 mL – MFCsCu 13 mL in series; parallel-both: MFCsCr 13 mL – MFCsCu 13 mL in parallel connection).

cathodes of MFCsCu with simultaneous Cd(II) reduction of $16.5 \pm 2.5\%$ in the connected MECsCd (Fig. 8A), compared to $45.5 \pm 0.7\%$ (Cu(II) reduction) and $21.3 \pm 0.1\%$ (Cd(II) reduction) in the volume-unchanged individual MFCsCu driving MECsCd system (Fig. 3A). Half-volume cathodes of individual MFCsCu were somewhat beneficial for voltage output (Fig. 8C) and maximal current density (Fig. 8D), both of which were favorable for Cu(II) reduction inside (Fig. 8A). However, a low circuit current of 0.1 ± 0.0 mA (Fig. 8B) together with a low applied voltage of 0.28 V (Fig. 8E) and a comparatively high cathode potential of -0.55 V (Fig. 8F) in the MECsCd self-driven by individual MFCsCu, explained the low Cd(II) reduction inside (Fig. 8A). Similarly and in the controls of single MFCsCr driving MECsCd system, $52.7 \pm 0.9\%$ of Cr(VI) in MFCsCr and $23.6 \pm 3.0\%$ of Cd(II) in MECsCd were respectively reduced (Fig. 8A). In the OCC controls, around 17.4% of Cr(VI) and 18.9% of Cu(II) were removed on the CR cathodes, higher than 3.6% for Cd(II) removal on the TS cathodes, mainly ascribed to the more efficient chemical adsorption in the former. Much less reduction of Cr(VI), Cu(II) and

Cd(II) in these controls aforementioned reflects the generally beneficial circuit current for simultaneous Cr(VI), Cu(II) and Cd(II) reduction in this system.

While increased current/voltage in parallel/serial stack MFCsCr and MFCsCu reasonably improved Cr(VI) and Cu(II) reduction inside, voltage reversal unavoidably occurred during MFCsCr and MFCsCu stack operation because of variability in the capacity for current generation by individual MFCsCr and MFCsCu in the stack [50,52]. This voltage reversal adversely affected power output (Fig. 8C and D), and somewhat detrimentally influenced Cr(VI) and Cu(II) reduction in this MFCsCr–MFCsCu–MECsCd self-driven system.

4. Conclusions

Compared to CR, TS was successfully used as the cathodes of MECsCd self-driven by stack MFCsCr and MFCsCu, providing a new active approach for not only harvesting MFCsCr and MFCsCu energy to power MECsCd, but also achieving simultaneous reduction of

Cr(VI), Cu(II) and Cd(II) with no requirement of external energy input. Amounting to $41.4 \pm 2.2\%$ of Cd(II), along with $56.4 \pm 0.5\%$ of Cr(VI) and $52.7 \pm 3.5\%$ of Cu(II) were reduced in MECs_{Cd} self-driven by MFCs_{Cr} 13 mL – MFCs_{Cu} 25 mL in serial connection. In addition, yields of 0.23 ± 0.04 mol Cd mol⁻¹ COD, 0.27 ± 0.03 mol Cr mol⁻¹ COD and 0.40 ± 0.05 mol Cu mol⁻¹ COD with simultaneous hydrogen production of 0.0022 ± 0.0001 m³ m⁻³ d⁻¹ were accordingly obtained.

While this self-driven MFCs_{Cr}-MFCs_{Cu}-MECs_{Cd} system described in this study represents a true sustainable process and is new to simultaneous recovery of Cr(VI), Cu(II) and Cd(II) from wastes, there are still many challenges to enable practical applications. The stack MFCs_{Cr} and MFCs_{Cu} coupled with the MECs_{Cd} might add up to the complexity of the treatment process, hence creating more challenges for process optimization and maintenance. The performance of each cell is interrelated, leading to the occurring of voltage reversal and thereby the increase of internal energy loss. Overcoming these limitations may call for further joint efforts in reactor engineering, material development and biological manipulation. Although a certain amount of Cr(VI), Cu(II) and Cd(II) has been successfully recovered in this system, the remaining Cr(VI), Cu(II) and Cd(II) ions in the effluent still need to be reduced in order for the requirement of national wastewaters release standard criterion. In view of these considerations, the development of continuous flow systems are needed to advance these new technologies, in which all reactors in a stack have the same hydraulic conditions and are fed with wastewaters containing the same concentrations of various metal species, and thereby decrease voltage reversal and internal energy loss [52]. Under this situation, however, the products recovered in MFCs_{Cr}, MFCs_{Cu} and MECs_{Cd} would be more or less impure and process optimization can thus necessarily avoid this occurrence. Further investigations in these directions are warranted.

Acknowledgments

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